Hz), 3.40 (dd, 1 H, CH, J = 5.8, 2.5 Hz), 7.12 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 158 (M^+, 22), 143 (23), 128 (8), 116 (65), 115 (100).

3-Phenyl-4,4-dimethyl-1-pentyne (1d): bp 51 °C (1 mm); IR 3307, 2114, 632 cm^{-1}; ^1H NMR δ 0.98 (s, 9 H, Me); 2.18 (d, 1 H, ≡CH, J = 2.7 Hz), 3.38 (d, 1 H, CH, J = 2.7 Hz), 7.23 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 172 (M^+, 5), 157 (11), 116 (46), 115 (23), 57 (100). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.39; H, 9.56.

3-Phenyl-3-methyl-1-pentyne (1e): bp 53 °C (0.8 mm); IR 3305, 2112, 636 cm^{-1}; ^1H NMR δ 0.87 (t, 3 H, Me, J = 7 Hz), 1.57 (s, 3 H, Me), 1.82 (q, 2 H, CH_2, J = 7 Hz), 2.33 (s, 1 H, ≡CH), 7.33 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 158 (M^+, 16), 143 (7), 129 (100), 128 (33), 115 (6). Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.88; H, 9.10.

3-Phenyl-3,4-dimethyl-1-pentyne (1f): bp 48 °C (0.4 mm); IR 3306, 2113, 635 cm^{-1}; ^1H NMR δ 0.75, 1.04 (2 d, 3 H each, Me, J = 6.5 Hz), 1.49 (s, 3 H, Me), 1.90 (m, 1 H, CH), 2.18 (s, 1 H, ≡CH), 7.22 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 172 (M^+, 11), 157 (15), 130 (66), 129 (100), 128 (55), 115 (21). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.82; H, 9.28.

3-Phenyl-3,4,4-trimethyl-1-pentyne (1g): bp 69-70 °C (1 mm); IR 3307, 2108, 632 cm^{-1}; ^1H NMR δ 0.98 (s, 9 H, Me), 1.65 (s, 3 H, Me), 2.28 (s, 1 H, ≡CH), 7.38 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 186 (M^+, 8), 171 (15), 156 (7), 143 (9), 130 (98), 129 (60), 128 (32), 115 (32), 57 (100). Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.11; H, 9.89.

1-Phenyl-1,2-butadiene:[19] IR 1950 cm^{-1}; ^1H NMR δ 1.73 (dd, 3 H, Me, J = 7, 3.2 Hz), 5.45 (m, 1 H, =C=CH, J = 6.5, 7 Hz), 6.03 (m, 1 H, =C=CH, J = 6.5, 3.2 Hz), 7.17 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 130 (M^+, 86), 115 (100).

1-Phenyl-1,2-pentadiene:[20] IR 1948 cm^{-1}; ^1H NMR δ 0.97 (t, 3 H, Me, J = 7 Hz), 1.98 (m, 2 H, CH_2, J = 7, 6.5, 3.2 Hz), 5.47 (m, 1 H, =C=CH), 6.07 (dt, 1 H, =C=CH, J = 6.5, 3.2 Hz), 7.14 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 144 (M^+, 57), 129 (100), 115 (54).

1-Phenyl-4-methyl-1,2-pentadiene:[21] IR 1947 cm^{-1}; ^1H NMR δ 1.02 (d, 6 H, Me, J = 6.5 Hz), 1.8-2.6 (m, 1 H, CH), 5.43 (t, 1 H, =C=CH, J = 6 Hz), 6.07 (dd, 1 H, =C=CH, J = 6, 3 Hz), 7.10 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 158 (M^+, 70), 143 (100), 129 (27), 128 (53), 116 (33), 115 (96).

1-Phenyl-4,4-dimethyl-1,2-pentadiene:[22] IR 1947 cm^{-1}; ^1H NMR δ 1.12 (s, 9 H, Me), 5.54 (d, 1 H, =C=CH, J = 6.4 Hz), 6.17 (d, 1 H, =C=CH, J = 6.4 Hz), 7.27 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 172 (M^+, 20), 157 (11), 116 (24), 115 (18), 57 (100).

1-Phenyl-3-methyl-1,2-pentadiene:[6] IR 1950 cm^{-1}; ^1H NMR δ 1.06 (t, 3 H, Me, J = 7.2 Hz), 1.80 (d, 3 H, Me, J = 3 Hz), 2.08 (dq, 2 H, CH_2, J. = 7.2, 3 Hz), 6.05 (m, 1 H, =C=CH, J = 3 Hz), 7.21 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 158 (M^+, 69), 143 (100), 129 (69), 128 (95), 115 (23).

1-Phenyl-3,4-dimethyl-1,2-pentadiene: IR 1949 cm^{-1}; ^1H NMR δ 1.03 (d, 6 H, Me, J = 6.5 Hz), 1.72 (d, 3 H, Me, J = 3 Hz), 1.8-2,6 (m, 1 H, CH), 6.03 (m, 1 H, =C=CH, J = 3 Hz), 7.15 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 172 (M^+, 46), 157 (49), 143 (16), 142 (17), 129 (100), 128 (39), 115 (14). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.34; H, 9.54.

1-Phenyl-3,4,4-trimethyl-1,2-pentadiene: IR 1950 cm^{-1}; ^1H NMR δ 1.13 (s, 9 H, Me), 1.80 (d, 3 H, Me, J = 2.8 Hz), 6.05 (q, 1 H, =C=CH, J = 2.8 Hz), 7.27 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 186 (M^+, 27), 171 (7), 143 (6), 130 (42), 129 (52), 128 (25), 115 (18), 57 (100). Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.09; H, 9.86.

2-Phenyl-2,3-hexadiene:[20] IR 1953 cm^{-1}; ^1H NMR δ 1.01 (t, 3 H, Me, J = 7 Hz), 2.04 (d, 3 H, Me, J = 3 Hz), 2.15 (m, 2 H, CH_2), 5.43 (m, 1 H, =C=CH), 7.22 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 158 (M^+, 71), 143 (100), 129 (90), 128 (89), 115 (25).

2-Phenyl-5,5-dimethyl-2,3-hexadiene:[14] IR 1955 cm^{-1}; ^1H NMR δ 1.08 (s, 9 H, Me), 2.05 (d, 3 H, Me, J = 2.8 Hz), 5.40 (q, 1 H, =C=CH, J = 2.8 Hz), 7.20 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 186 (M^+, 35), 171 (15), 156 (9), 143 (11), 130 (50), 129 (41), 115 (21), 57 (100).

(S)-3-Phenyl-1-butyne [(S)-(+)-1a]. Following the general procedure given above, (R)-(-)-**2a** (1.53 g, 11.5 mmol) in tetrahydrofuran (15 mL) was allowed to react with 2 equiv of the cuprate $PhCu{\cdot}MgBr_2{\cdot}LiBr$. After the usual workup, the reaction mixture afforded a fraction [yield, 1.46 g (97%)] containing compound **1a** (80%) and 1-phenyl-1,2-butadiene (20%). Purification by preparative GC (SE-30) yielded pure (S)-(+)-**1a** (0.96 g, 64%) showing bp 69 °C (17 mmHg); $[\alpha]^{25}_D$ +3.91 (c 10.4, heptane) [optically pure (S)-(+)-**1a** is reported to have $[\alpha]^{25}_D$ +21.8 (heptane)].[2]

Pure samples of (S)-(+)-**1a** having $[\alpha]^{25}_D$ +3.70 (heptane) and $[\alpha]^{25}_D$ +3.82 (heptane) were obtained also by repeating the same reaction two times again.

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Registry No. (±)-**1a**, 86738-23-0; (S)-(+)-**1a**, 109279-81-4; (±)-**1b**, 109182-83-4; (±)-**1c**, 109182-84-5; (±)-**1d**, 109182-85-6; (±)-**1e**, 109182-86-7; (±)-**1f**, 109182-87-8; (±)-**1g**, 109182-88-9; (±)-**2a**, 109279-75-6; (R)-(-)-**2a**, 94137-75-4; (±)-**2b**, 109182-79-8; (±)-**2c**, 109182-80-1; (±)-**2d**, 109279-76-7; (±)-**2e**, 109279-77-8; (±)-**2f**, 109182-81-2; (±)-**2g**, 109279-78-9; (±)-**2h**, 109279-79-0; (±)-**2i**, 109182-82-3; (±)-**3a**, 70000-51-0; (±)-**3b**, 109182-89-0; (±)-**3c**, 109182-90-3; (±)-**3d**, 109279-80-3; (±)-**3e**, 109182-91-4; (±)-**3f**, 109182-92-5; (±)-**3g**, 109182-93-6; (±)-**3i** (R = Et), 109182-94-7; (±)-**3i** (R = t-Bu), 109182-95-8; (S)-(-)-4, 2914-69-4; (S)-**5**, 73647-37-7.

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Stereoselective Reduction of *gem*-Dichlorocyclopropanes by Potassium Diphenylphosphide

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Although *gem*-dibromocyclopropanes react readily with potassium dimethyl phosphite $[K^+P(O)(OMe)_2^-]$ to give reduced products with high stereoselectivity when the halogens are nonequivalent, the corresponding dichloro compounds are quite inert.[2] As part of an investigation into the interaction of nucleophilic reagents with halocyclopropanes, the reaction of *gem*-dichlorocyclopropanes with potassium diphenylphosphide $[K^+PPh_2^-]$ has been examined. Diphenylphosphide ion is a more reactive phosphanion than is dimethyl phosphite ion and rapidly reduces dibromocyclopropanes[3] to their monobromides, which under irradiation react further to give the products of $S_{RN}1$ substitution.[3,4] The aim of this study was to determine whether dichlorocyclopropanes followed a similar pathway.

When 7,7-dichlorobicyclo[4.1.0]heptane (**1a**) was stirred in the dark for 4 h in liquid ammonia with potassium

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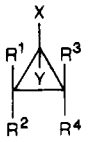
Table I. Reaction of 1a-g with Diphenylphosphide Ion

entry	substr[a]	[PPh_2^-], M	solvent	reactn time, h	substr remaining, %	2, %	3, %
1	**1a**	0.075	NH_3[b]	4	36	45	1
2	**1a**	0.15	NH_3	4	26	62	1
3	**1a**	0.3	Me_2SO	4	0	84	4
4	**1a**	0.11	Me_2SO	4	10	69	5
5	**1a**	0.2	Me_2SO	1	0	83	5
6	**1b**	0.2	Me_2SO	1	0	81	6
7	**1c**	0.2	Me_2SO	1	0	74	15
8	**1d**	0.2	Me_2SO	1	0	73	14
9	**1e**	0.2	Me_2SO	1	0	74	20
10	**1f**	0.2	Me_2SO	1	0	99	
11	**1g**[c]	0.2	Me_2SO	1	0	10	4
12	**1g**	0.075	NH_3	4	0	69	19

[a] The substrate concentration was 0.025 M for experiments conducted in liquid ammonia and 0.1 M for experiments carried out in Me_2SO. [b] NH_3 refers to liquid ammonia at −33 °C. [c] **6g** (41%) was isolated after oxidative workup.

diphenylphosphide (Table I, entry 1), the major product was *trans*-7-chlorobicyclo[4.1.0]heptane (**2a**). It was accompanied by a small amount of the cis isomer **3a** and the starting material, but the direduced product **4a** was not obtained. The reaction was not affected by the addition of di-*tert*-butyl nitroxide, implying that nonradical intermediates such as those suggested previously for the reduction of dibromocyclopropanes are involved.[2] Irradiation of the reaction mixture with 350-nm light for 4 h did not promote substitution of the remaining halogen, unlike its dibromo analogue.[3] A modest improvement in the yield of **2a** (entry 2) was obtained when the concentration of diphenylphosphide ion was doubled, but starting material was also returned.



1: X = Y = Cl
2: X = H; Y = Cl
3: X = Cl; Y = H
4: X = Y = H
5: X = Y = PPh_2
6: X = Y = P(O)Ph_2
a: $R^1, R^3 = (CH_2)_4$; R^2, R^4 = H
b: $R^1, R^3 = (CH_2)_6$; R^2, R^4 = H
c: $R^1 = CH_3(CH_2)_3$; R^2, R^3, R^4 = H
d: $R^1 = CH_3(CH_2)_5$; R^2, R^3, R^4 = H
e: $R^1, R^2, R^3 = CH_3$; R^4 = H
f: $R^1, R^2, R^3, R^4 = CH_3$
g: R^1 = Ph; R^2, R^3, R^4 = H

The reduction however proceeded to completion in Me_2SO. When 3 equiv of diphenylphosphide ion was treated with **1a** (entry 3), the starting material was fully consumed and the trans isomer **2a** (84%) was obtained as the major product. The stereoselectivity in this solvent was somewhat lower than in liquid ammonia, and a small yield of the cis isomer **3a** was also obtained. When the excess of diphenylphosphide ion was reduced to only 10%, some starting material was recovered even after a reaction time of 4 h, but when 2 equiv of the phosphanion was employed (entry 5), the reaction was complete in 1 h. All further experiments were carried out with this ratio of phosphanion to dichloride.

The dichlorobicyclononane **1b** also underwent reduction to give the trans monochloride **2b** (81%) as the major product, accompanied by some of the cis isomer **3b** (6%). Similarly, when **1c** was treated with diphenylphosphide ion in Me_2SO, the trans monochloride **2c** (74%) was the major product. When the reaction was carried out with the hexyl-substituted cyclopropane **1d** (entry 8), the ratio of the monochlorides **2d** to **3d** was 5:1. The trisubstituted cyclopropane **1e** was reduced cleanly but afforded a slightly lower excess of the trans isomer **2e** than from the other substrates. The tetramethylcyclopropane **1f**, in which both halogens are equivalent, was smoothly reduced to the monochloride by the procedure. In none of the above cases did starting material remain or were the products of overreduction detected.

Table II. Isolated Yields and ^1H NMR Coupling Constants from the Reaction of 1a-e with Diphenylphosphide Ion[a]

substr	(2 + 3), %	ratio 2 to 3[b]	J_{trans}, Hz	J_{cis}, Hz
1a	76	15	3.4	7.7
1b	77	17	3.4	7.7
1c	76	5	3.5	7.7
1d	80	6	3.4	7.8
1e	62	4	4.1	7.9
1f	76			

[a] Carried out in Me_2SO using 1.5 equiv of diphenylphosphide ion (see the Experimental Section). [b] Calculated from the ^1H NMR spectrum (300 MHz).

1,1-Dichloro-2-phenylcyclopropane (**1g**) gave somewhat different results on treatment with diphenylphosphide ion. In Me_2SO (entry 11), in addition to small yields of **2g** and **3g**, the bis(phosphine) **5g** was obtained and isolated as **6g** after oxidative workup. This substitution product seems likely to be formed by an elimination–addition sequence.[5] Of the substrates examined, substitution occurs only in the case of **1g**, where elimination of the halogens is conjugatively favored. Moreover, the yield of **6g** is not reduced by the addition of the radical scavenger di-*tert*-butyl nitroxide (5 mol %), suggesting that substitution by a homolytic pathway (such as by the $S_{RN}1$ process)[4,6] is unlikely. When the reaction was repeated in liquid ammonia, the substitution product was not obtained, and the monochlorides **2g** and **3g** (ratio 3.6:1) were formed in 88% overall yield.

The procedure was also examined from a preparative view.[7] Table II lists the combined yields of pure, distilled monochlorides **2** and **3** from preparative runs, typically starting with about 3 g of the dichloride and a reaction time of 1 h.

Assignment of Stereochemistry. The identities of the reduced products **2** and **3** were established, where possible,

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by comparison with samples obtained by other routes[8,9] and confirmed by the ^1H NMR (300-MHz) spectrum.[9-11] ^1H NMR coupling constants J_{trans} and J_{cis} are listed in Table II and were derived either by direct means or from decoupling experiments.

Experimental Section

General Procedures. Analytical GLC was performed on a Perkin-Elmer 990 gas chromatograph equipped with a flame-ionization detector. The column used was a 55 m × 0.5 mm SP 2100 SCOT capillary, temperature programmed between 50 and 240 °C. ^1H NMR spectra were recorded in $CDCl_3$ on either a JEOL JNM-PMX 60 (60-MHz) or a Bruker CXP-300 (300-MHz) spectrometer. ^{13}C NMR spectra were determined on a Bruker WP-80 DS instrument. Mass spectra were determined on an AEI MS-3074 spectrometer at 70 eV in electron impact mode.

Starting Materials. *gem*-Dichlorocyclopropanes[13-16] were prepared by phase-transfer methods as previously described.[17,18] Ammonia was distilled from sodium prior to use. Me_2SO was distilled from calcium hydride and stored over molecular sieves under an atmosphere of nitrogen. Potassium *tert*-butoxide (Fluka) was used as received. Diphenylphosphine was prepared by the method of Gee et al.[19]

Typical Procedure. Diphenylphosphine (372 mg, 2.0 mmol) was added by syringe to a stirred solution of potassium *tert*-butoxide (224 mg, 2.0 mmol) in Me_2SO (10 mL) under N_2. After 10 min of stirring, 7,7-dichlorobicyclo[4.1.0]heptane (165 mg, 1.0 mmol) was added. The mixture was allowed to stir for 1 h and then was poured into water and extracted twice with petroleum spirit (bp 30-40 °C). The combined extracts were washed with water and dried. After the addition of an internal standard (2-chlorotoluene), the mixture was quantitatively examined by GLC. All yields were corrected for the detector responses.

Experiments in liquid ammonia were carried out at reflux on the same scale, except that the volume of liquid ammonia was 40 mL. After the reaction was complete, chilled (-40 °C) ether was added, and the reaction mixture was quenched by the cautious addition of ammonium nitrate (0.75 g). The ammonia was allowed to evaporate, and the mixture was diluted with water. The ether phase was washed with water, dried, and examined as before.

1,1-Bis(diphenylphosphinyl)-2-phenylcyclopropane. Dichloride **1g** (187 mg, 1.0 mmol) was added to a solution of potassium diphenylphosphide (2.0 mmol) in Me_2SO (10 mL) prepared as before. The mixture was stirred at room temperature for 1 h and then worked up as before and examined by GLC after the addition of an internal standard. The solvent was then removed, and 30% aqueous hydrogen peroxide (30 mL) was added cautiously in portions to a vigorously stirred solution of the residue in CH_2Cl_2 (30 mL). After 15 h of stirring, the organic phase was separated, washed with water, and dried. The crude product was subjected to flash chromatography on silica gel (25% ether/CH_2Cl_2) to afford the phosphine oxide **6g**: 210 mg; mp 210-211 °C; ^{13}C NMR δ 15.2 (t), 26.6 (t, J_{P-C} 78 Hz), 29.1 (d), 125-133 (unresolved); ^1H NMR (60 MHz) δ 1.7-3.2 (m, 3 H), 6.6-8.1 (m, 25 H); MS, *m/z* (relative intensity) 518 (M^+, 100), 412 (28), 288 (8), 201 (12); exact mass *m/z* 518.1564, calcd for $C_{33}H_{28}O_2P_2$ *m/z* 518.1565.

Preparative Experiments. The following example is illustrative. Diphenylphosphine (5.58 g, 30 mmol) was added dropwise to a stirred solution of potassium *tert*-butoxide (3.37 g, 30 mmol) in Me_2SO (50 mL) under N_2. The flask was immersed in a bath of cold water during both the addition and the subsequent steps. After 15 min of stirring, 7,7-dichlorobicyclo[4.1.0]heptane (3.30 g, 20 mmol) was added dropwise, and the mixture was allowed to stir for 1 h. After this time, it was poured into water (100 mL) and extracted with pentane (2 × 25 mL). The combined extracts were washed several times with water. The dried extracts were concentrated through a Vigreux column (15 cm), and the residue was distilled with a short-path apparatus to afford a mixture of **2a** and **3a**: 1.98 g, 76%; bp 60-61 °C (10 mmHg) [lit.[8] bp 78 °C (16 mmHg)].

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Registry No. **1a**, 823-69-8; **1b**, 6498-44-8; **1c**, 3722-08-5; **1d**, 5685-42-7; **1e**, 20202-10-2; **1f**, 3141-45-5; **1g**, 2415-80-7; **2a**, 18688-22-7; **2b**, 24266-06-6; **2c**, 109125-04-4; **2d**, 64139-65-7; **2e**, 35731-78-3; **2f**, 14123-41-2; **2g**, 17651-00-2; **3a**, 18688-21-6; **3b**, 24266-07-7; **3c**, 109125-05-5; **3d**, 64139-64-6; **3e**, 35731-79-4; **3g**, 17650-99-6; **6g**, 109125-06-6; potassium diphenylphosphide, 15475-27-1.

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Exceptionally Slow Reduction of Phenylmalonic Acid by Borane-THF via Cyclic (Phenylmalonoxy)borane

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The remarkable ease with which carboxylic acids, both aliphatic and aromatic, are reduced by borane-tetrahydrofuran (BH_3·THF) has been previously described.[1,2]

$$RCOOH \xrightarrow{BH_3\cdot THF} \underset{>95\%}{RCH_2OH}$$

R = alkyl or aryl

Brown and co-workers have recently established the details of the borane reduction mechanism which must proceed through the intermediate formation of monoacyloxyborane, either formed directly from the carboxylic acid and borane or formed by a redistribution reaction of diacyloxyborane with borane.[3]

During synthesis of the labeled new anticonvulsant [^{14}C]felbamate, we have observed that the reduction of phenylmalonic acid (**1**) even with an excess of borane-tetrahydrofuran is unusually slow. This reaction proceeded sluggishly at 0 °C, requiring 16 h to yield only 35% of 2-phenyl-1,3-propanediol and unreacted starting material.[4] Moreover, the yield was not enhanced by the use of bo-

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